

Characterization of dyes biosorption on fungal biomass

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The characterization of the dyes adsorption on granular particles of *Cunninghamella elegans* inactivated biomass is reported. The adsorption process regarded a dye bath for wool and each of the three dyes composing it: Acid Blue 62, Acid Red 266 and Acid Yellow 49. Adsorption isotherms and adsorption kinetics were assessed together with the effect of biomass particle size. The maximum adsorption capacity of lyophilised biomass with respect to Acid Red 266, Acid Blue 62, Acid Yellow 49 and to the model wastewater were 500, 230, 230 and 390 mg_{dye}/g_{DM}, respectively. A mutual interference among adsorbed dyes resulted. The adsorption kinetics for the Acid Blue 62 resulted of the first order type and the first order parameter was $3.6 \pm 1.1 \text{ h}^{-1}$.

1. Introduction

Wastewaters contaminated by dyes represent a relevant issue associated with several industries. Dyes, even at very low concentrations, reduce wastewater transparency and oxygen solubility and are often toxic and recalcitrant; moreover, these chemicals are toxic, carcinogenic or mutagenic for various organisms (Mathur and Bhatnagar, 2007). In addition, coloured streams are characterized by large fluctuations of composition, pH and temperature (Hai et al., 2007). Physical and chemical remediations of coloured wastewaters are not always effective and often very expensive (Crini, 2006; Hai et al., 2007). Preliminary assessment of the wastewaters remediation by sorption of dyes on microbial biomasses demonstrated the potential of this process (Crini, 2006). The main features of the biosorption processes are the good adsorption capacity and cost effectiveness (Aksu, 2005). The processes become less expensive when biomasses are the waste products of industrial processes (Maurya et al., 2006). Recent studies are mainly focused on the characterization of processes regarding single dye solutions at low concentration. Only few studies regard multi-dye solutions emulating industrial effluents (Aksu, 2005; Prigione et al., 2008a and 2008b) and the mechanisms responsible for the dye(s) biosorption are still under study. Typically, uptake of the pollutants take place at the cell wall and many biotic and abiotic factors affect it (Aksu, 2005; Casieri et al., 2008).

The present contribution regards the characterization of the dye sorption process by

means of granular lyophilized biomass of *Cunninghamella elegans*. Tests were carried out with a typical dye bath for wool and with each of the three dyes composing it: Acid Blue 62, Acid Red 266 and Acid Yellow 49. The investigation was focused on the assessment of adsorption isotherms and of adsorption kinetics. Ecotoxicity tests were also carried out on the treated model wastewater.

2. Materials, apparatus and procedures

2.1 Biomass and dyes

The biomass of *Cunninghamella elegans* produced according to Prigione et al. (2008a and 2008b) was inactivated and lyophilised. The granular material was sieved in the size ranges 600-1000, 300-600, 150-300 and less than 150 μm .

Tests were carried out with a model wastewater mimicking a dye bath for wool (Prigione et al., 2008b) and with solutions of the single dyes components the wastewater: Acid Blue 62 (ABu62), Acid Red 266 (AR266) and Acid Yellow 49 (AY49). Acid dyes in the model wastewater were added up to 900 mg/L (mass ratio 1:1:1) in 2g/L Na_2SO_4 aqueous solution at pH 5. The initial concentration of single dye solutions ranged between 10 and 1000 mg/L. The dye concentration in monocomponent solutions was measured at 636 nm (ABu62), 495 nm (AR266) and 401 nm (AY49). The concentration of each dye in the model wastewater was assessed by working out the absorbance spectrum of the mixture.

Pseudokirchneriella subcapitata (Korshikov) Hindak (planktonic freshwater algae) was used to assess the toxicity of the decolourized solutions (standard UNI EN ISO 8692:2005).

2.2 Experimental apparatus

Decolourization tests aimed at the assessment of the adsorption isotherm and of the adsorption capacity (see § 2.3) were carried out batchwise in 30-100 mL Erlenmeyer flasks.

The assessment of the decolourization kinetics was carried out in the apparatus sketched in Fig. 1. A tubular vessel (8 mm ID, 60 mm long) was equipped with a gear pump, a 100 mL mixed tank and an on-line flow cell (720 μL) housed in the spectrophotometer (Cary 50, Varian Inc.). The liquid was circulated by means of the pump (VG 1000 digit, Verder). The tubular vessel was packed with 300-600 μm lyophilized biomass (0.03-0.05 g_{DM}) mixed with 300 μm glass beads to improve uniform liquid flow throughout

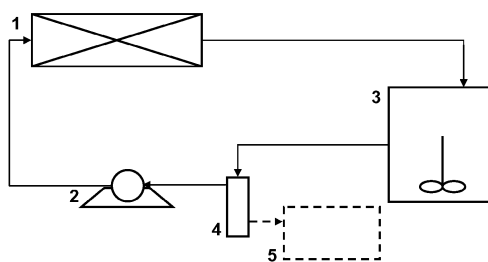


Fig. 1. Apparatus for the assessment of the adsorption kinetics. 1- packed bed, 2- gear pump, 3- stirred tank, 4- flow cell, 5- spectrophotometer.

the vessel. Single dye solutions were characterised by measuring absorbance at the proper wavelength by the on-line flow cell.

2.3 Procedures

Three types of tests were carried out.

A-type) Adsorption isotherms. A fixed amount of biomass was mixed in Erlenmeyer flasks with a known amount of solution and incubated at room temperature under mixing. Solution sampling was regularly carried out and the dye(s) concentration was measured till the equilibrium was achieved. Adsorbed amount of dye was calculated working out the difference between the initial and the final concentration in the liquid phase. Each test was carried out in triplicate.

B-type) Adsorption capacity. The procedure is similar to the A-type experiments. Provided that biomass and liquid phase reached the dye(s) repartition equilibrium, the liquid was replaced with a known volume of the fresh solution and the dye uptake characterization continued. The solution refresh was repeated until no more dyes were adsorbed on the biomass.

C-type) Adsorption kinetics. Tests were carried out with the device reported in Fig. 1 and in agreement with the procedure developed by Russo et al. (2008) and regarded mono-dye solutions. The time-resolved measurements of the optical absorbance – at the pre-fixed wavelength – of the liquid phase were worked out to assess the rate of adsorption of a single dye. The following assumptions were verified: i) well mixing of the liquid phase in the tank; ii) the packed bed operated as a differential unit; iii) negligible external mass transfer resistance in the packed bed. Hypothesis iii) holds under the conditions

$$r_{ads} \ll K_l c \frac{6(1-\varepsilon)}{d_p} \quad (1)$$

where r_{ads} is the dye adsorption rate, c the dye concentration in the liquid phase, K_l the mass transfer coefficient, ε the local voidage and d_p the diameter of the biomass particle. The interphase mass transfer coefficient K_l was calculated according to Geankoplis (1993) for liquid phase flowing across a packed bed. Eq. (1) was verified for flow rate between 30 and 60 mL/min, initial dye concentration between 5 and 100 mg/L and 300-600 μm particles. Tests were carried out at flow rate of 43 mL/min so that K_l resulted about 600 h^{-1} .

3. Results

Preliminary study was performed to investigate the effect of the particle size on adsorption capacity. A-type tests regarded the pH 5 wastewater model at overall concentration of 300 mg/L of lyophilized biomass with different particle diameter. The equilibrium conditions did not change, provided that the particles diameter was larger than 150 μm , and were: adsorbed dye concentration $29.1 \pm 0.1 \text{ mg}_{\text{dye}}/\text{g}_{\text{DM}}$, liquid phase dye concentration $0.46 \pm 0.4 \text{ mg/L}$. A slight difference was observed for the finest particles (less than 150 μm): $29.6 \text{ mg}_{\text{dye}}/\text{g}_{\text{DM}}$, 0.21 mg/L .

The *P. subcapitata* toxicity tests pointed out a remarkable reduction of toxicity after

biosorption treatments (data not shown), whatever the biomass particles size.

Systematic tests were focused on granular biomass sieved between 300 and 600 μm . The range has been selected as a good candidate to be adopted in adsorbers of fixed bed typology.

Figure 2 shows results of tests carried out in agreement with the A-type procedure. Equilibrium data regard ABu62 - initial pH=5, room temperature - and are reported in terms of dye concentration in the liquid phase (c_{eq}) and concentration on the biomass (w_{eq}). Data were worked out in agreement with the Langmuir model:

$$w_{eq} = w_{max} \frac{kc_{eq}}{1 + kc_{eq}} \quad (2)$$

The data regression gave $w_{max}=452 \text{ g}_{\text{dye}}/\text{g}_{\text{DM}}$ and $k=0.01 \text{ L}/\text{g}_{\text{dye}}$.

Figure 3 reports results regarding the assessment of the maximum adsorption capacity carried out in agreement with the B-type procedure. The maximum adsorption capacity of the biomass as regards the single dye solutions was (Fig. 3A): 230 $\text{mg}/\text{g}_{\text{DM}}$ for ABu62 and AY49, and 500 $\text{mg}/\text{g}_{\text{DM}}$ for AR266. A particular affinity of the biomass was observed for AR266. As regards the model wastewater, Fig. 3B shows the adsorption capacity with respect to the dyes mixture (maximum 390 $\text{mg}/\text{g}_{\text{DM}}$) and to each component.

The comparison of data reported for ABu62 in Fig. 2 and Fig. 3A confirms the role of the experimental procedure in the assessment of the equilibrium conditions. In particular, equilibrium data in Fig. 3A reflects the typical breakthrough behaviour of a fixed bed.

Comparing data in Fig. 3A and 3B, it appears that the maximum adsorption capacity of the biomass with respect to the single dye reduces when dyes are mixed together. Adsorption of AR266 was more rapid than that of AY49 and ABu62 (data not shown) so the saturation, reached refreshing the system with model wastewater, was actually characterised by saturation with respect to AY49 and ABu62 while the biomass was not yet saturated with respect to AR266. These results suggest that, among the active sites

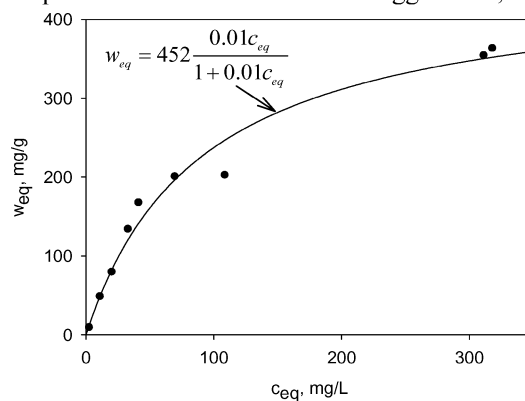


Fig. 2. Adsorption isotherm of ABu62. Initial pH=5, equilibrium pH=6÷7. Particle size 300-600 μm . Room temperature.

involved in the adsorption phenomena, some sites may interact with all the three dyes. Therefore, the higher affinity of the biomass towards AR266 and the faster adsorption kinetics of AR266 likely reduce the adsorption capacity of the biomass towards both AY49 and ABu62.

Time-resolved measurements of dye concentration from two C-type tests are reported in Fig. 4. The data refer to runs carried out at room temperature with a solution (pH 6–7) of ABu62 at initial concentration of dye (c_0) of 20 and 50 mg/L. The analysis of the time-series from all the tests carried out ($5 < c_0 < 100$ mg/L) suggested that the decolourization rate increases with the initial dye concentration. In particular, a first order kinetics may be assumed:

$$r_{ads} = K(c - c_{eq}) \quad (3)$$

where r_{ads} is dye adsorption rate for unit volume of liquid phase (mg_{dye}/L h), and K the

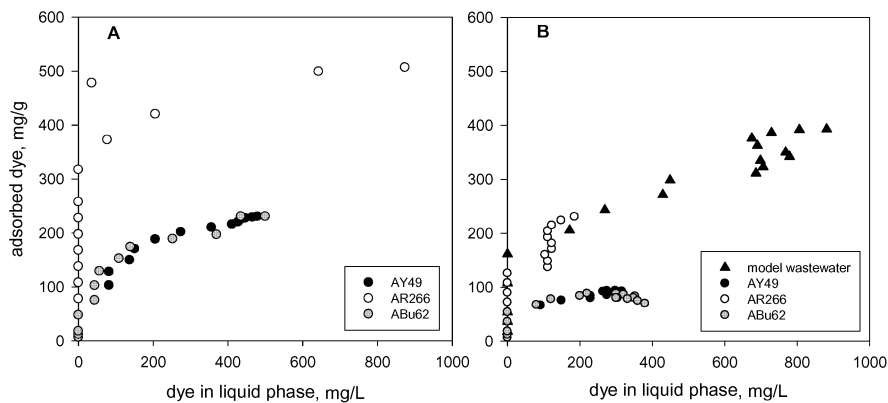


Fig. 3. Maximum adsorption capacity of lyophilised biomass for the three investigated dyes (A) and for the model wastewater (B), in agreement with the B-type tests. Particle size 300–600 μm . Room temperature. Initial pH 5.

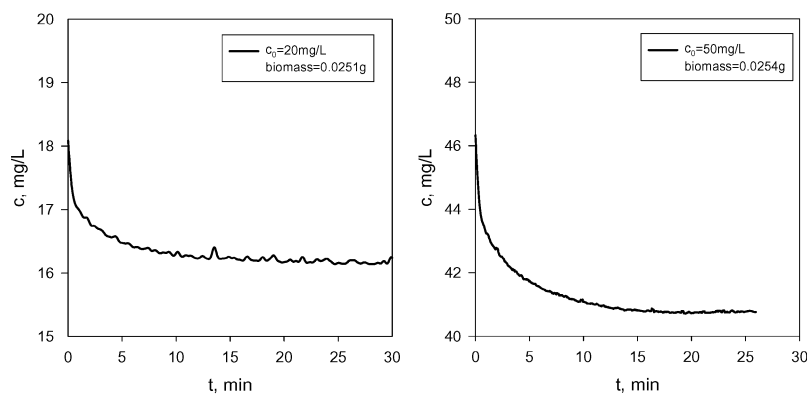


Fig. 4. Adsorption kinetics for ABu62. Room temperature, pH 6–7, tank volume 100 mL.

first order coefficient accounting for both intra-particle diffusion resistance and intrinsic adsorption kinetic. Under proper operating conditions the overall behaviour of the device (Fig.1) closely approached that of a stirred batch adsorber. Accordingly, the adsorption rate was assessed by regressing the time course of c through the mass balance on the dye extended to the liquid phase:

$$V_T \frac{dc}{dt} = V_B K (c - c_{eq}) \quad (4)$$

$t = 0, c = c_0$

where V_T and V_B are the tank and the packed bed volumes, respectively. The c_{eq} was estimated by means of the mass balance on the dye extended to the loop:

$$M \cdot w_{eq} = (V_T + V_B) \cdot (c_0 - c_{eq}) \quad (5)$$

where M is the biomass packed into the column. Working out the measured dye concentration through eq.s (2)-(5) K was assessed at $3.6 \pm 1.1 \text{ h}^{-1}$.

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